QM II Serie 9 Sebastian Keller

(1)

i) $$Z = \operatorname{tr}\left(e^{-\beta H^{vib}}\right) = \sum_n e^{-\beta\hbar\omega(n+\frac{1}{2})}$$

$$= \frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}}$$

$$\boxed{\Rightarrow U} = -\frac{\partial}{\partial\beta}\log Z = -\frac{\partial}{\partial\beta}\left[(-\beta\hbar\omega/2) - \log\left(1-e^{-\beta\hbar\omega}\right)\right]$$

$$= \frac{\hbar\omega}{2} + \frac{\partial}{\partial\beta}\log\left(1-e^{-\beta\hbar\omega}\right) = \frac{\hbar\omega}{2} + \frac{1}{1-e^{-\beta\hbar\omega}}\cdot e^{-\beta\hbar\omega}\cdot\hbar\omega$$

$$= \hbar\omega\left(\frac{1}{2} + \frac{e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}\right)$$

$$\boxed{\Rightarrow C_V^{vib}} = -\frac{1}{k_B T^2}\frac{\partial}{\partial\beta}U = \frac{-\hbar\omega}{k_B T^2}\frac{\partial}{\partial\beta}\left(\frac{1}{2} + \frac{e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}\right)$$

$$= \frac{-\hbar\omega}{k_B T^2}\left(\frac{-\hbar\omega e^{-\beta\hbar\omega}\left(1-e^{-\beta\hbar\omega}\right) - e^{-\beta\hbar\omega}\cdot\hbar\omega e^{-\beta\hbar\omega}}{\left(1-e^{-\beta\hbar\omega}\right)^2}\right)$$

$$= -k_B\left(\frac{\hbar\omega}{kT}\right)^2\cdot\left(\frac{-e^{-\beta\hbar\omega} + e^{-2\beta\hbar\omega} - e^{-2\beta\hbar\omega}}{\left(1-e^{-\beta\hbar\omega}\right)^2}\right) = k_B\left(\frac{\hbar\omega}{kT}\right)^2\frac{e^{-\beta\hbar\omega}}{\left(1-e^{-\beta\hbar\omega}\right)^2}$$

$$= k_B\left(\frac{\hbar\omega}{kT}\right)^2\frac{e^{\frac{\hbar\omega}{kT}}}{\left(e^{\frac{\hbar\omega}{kT}}-1\right)^2} \quad \left(\text{Erweitert mit } e^{2\beta\hbar\omega}\right)$$

T klein

$$\approx k_B\left(\frac{\hbar\omega}{kT}\right)^2 e^{-\frac{\hbar\omega}{kT}} \longrightarrow 0 \quad (T\to 0)$$

Limes für $\beta \to 0$, $T \to \infty$

$$C_V^{vib} = k_B (\beta \hbar \omega)^2 \frac{1 + \beta \hbar \omega + \mathcal{O}(\beta^2)}{(\beta \hbar \omega + \mathcal{O}(\beta^2))^2}$$

$$= k_B (\beta \hbar \omega)^2 \frac{1 + \hbar \omega \beta + \mathcal{O}(\beta^2)}{(\beta \hbar \omega)^2 + \beta \hbar \omega\, \mathcal{O}(\beta^2) + \mathcal{O}(\beta^2)}$$

$$= k_B \frac{1 + \hbar \omega \beta + \mathcal{O}(\beta^2)}{1 + \mathcal{O}(\beta) + \mathcal{O}(\beta^2)} \xrightarrow{\beta \to 0} \underline{\underline{k_B}}$$

$$\Rightarrow \underline{\underline{\lim_{T \to \infty} C_V^{vib} = k_B}}$$

ii) $$Z = \sum_{\ell=0}^{\infty} (2\ell+1)\, e^{-\frac{\hbar^2 \beta \ell(\ell+1)}{2\Theta}}$$ ist nicht analytisch berechenbar

• Sei T klein, β gross, dann

$$Z \approx 1 + 3 e^{-\frac{\hbar^2\beta}{\Theta}} + \underbrace{\ldots}_{\text{klein}}$$

$$\log Z = \log\left(1 + 3 e^{-\frac{\hbar^2\beta}{\Theta}}\right) \approx 3 e^{-\frac{\hbar^2\beta}{\Theta}} = (*)$$

$$\frac{\partial^2}{\partial\beta^2}(*) = 3\left(\frac{\hbar^2}{\Theta}\right)^2 e^{-\frac{\hbar^2\beta}{\Theta}} = (**)$$

$$\frac{(**)}{k_B T^2} = 3 k_B \left(\frac{\hbar^2}{k_B T}\right)^2 e^{-\frac{\hbar^2}{k_B T \Theta}} = 12\, k_B \left(\frac{\hbar^2}{2 k_B T}\right)^2 e^{-\frac{\hbar^2}{k_B T\Theta}}$$

$$\Rightarrow \quad C_V^{rot} = \frac{1}{k_B T^2}\frac{\partial^2}{\partial\beta^2}\log Z = 12\, k_B\left(\frac{\hbar^2}{2k_BT}\right)^2 e^{-\frac{\hbar^2}{k_BT\Theta}}, \quad T \text{ klein}$$

• Sei T gross, β klein

$$Z = \sum \ldots \approx \int_0^\infty (2\ell+1)\, e^{-\frac{\hbar^2\beta\ell(\ell+1)}{2\Theta}}\, d\ell \overset{\text{Mathematica}}{=} \frac{2\Theta}{\beta\hbar^2}$$

Berechne jetzt $\frac{1}{k_BT^2}\frac{\partial^2}{\partial\beta^2}\left(\frac{2\Theta}{\beta\hbar^2}\right)$

log

turn page

$$\frac{\partial^2}{\partial\beta^2}\log z = \frac{\partial}{\partial\beta}\,\frac{\partial_\beta z}{z} = \frac{\partial_\beta^2 z\cdot z - (\partial_\beta z)^2}{z^2}$$

$$\left[\; z = \frac{2\theta}{\beta\hbar^2},\quad \partial_\beta z = -\frac{2\theta}{\beta^2\hbar^2},\quad \partial_\beta^2 z = \frac{4\theta}{\beta^3\hbar^2}\;\right]$$

$$= \frac{\frac{4\theta}{\beta^3\hbar^2}\cdot\frac{2\theta}{\beta\hbar^2} - \frac{4\theta^2}{\beta^4\hbar^4}}{\frac{4\theta^2}{\beta^2\hbar^4}} = \frac{\frac{4\theta^2}{\beta^4\hbar^4}}{\frac{4\theta^2}{\beta^2\hbar^4}} = \frac{1}{\beta^2}$$

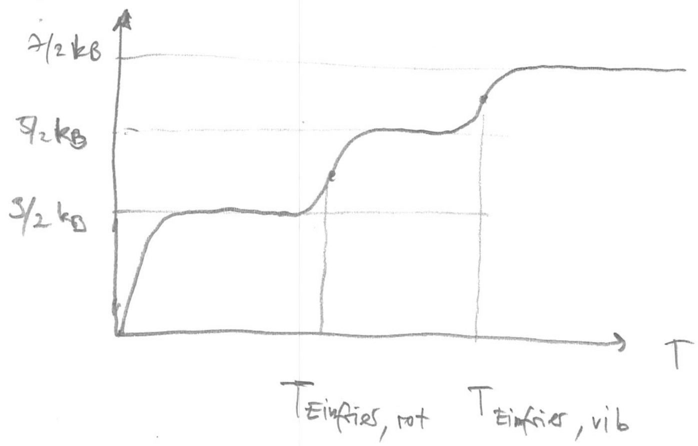
$$\Rightarrow \frac{1}{k_B T^2}\frac{\partial^2}{\partial\beta^2}\log z = k_B\beta^2\cdot\frac{1}{\beta^2} = k_B$$

$$\Rightarrow \underline{\underline{\lim_{T\to\infty} c_V^{rot} = k_B}}$$

Es gibt 2 vibronische Freiheitsgrade. (Wieso?)

(2 Kerne $\to 3\cdot 2 = 6$ Freiheitsgrade
= 3 Translation, 2 Rotation,
1 Vibration ?)

iii)



$\hookrightarrow \Rightarrow$ Solve$\left(c_V^{vib}(T) == \frac{1}{2}k_B\right)$

$\hookrightarrow$ Solve$\left(c_V^{rot}(T) == \frac{1}{2}k_B\right)$

(2) i) $$H(\phi, A) = \frac{1}{2m}(p - eA)^2 - \frac{e^2}{|x|} + e\phi$$

$$H(-E(t)x, 0) = H_R \qquad H(0, A) = H_K$$

$$\tilde{\phi} \quad \tilde{A}$$

Use: $\cdot\; A(t) = -\int_{-\infty}^{t} dt'\, E(t') \Rightarrow \dot{A}(t) = -E(t)$

$\cdot\; \Lambda(x,t) = -A(t)\cdot x$

$\cdot\; H$ (not H_K, H_R) is invariant under Gauge transforms

Gauge transform: $$A \to \tilde{A} = A + \vec{\nabla}\Lambda = A - A = 0$$

$$\phi \to \tilde{\phi} = \phi - \partial_t \Lambda = \phi - E(t)x$$

$$\Rightarrow \tilde{H} = \frac{1}{2m}(p)^2 - \frac{e^2}{|x|} + e(\phi - E(t)x)$$

$\Rightarrow \tilde{H}(0, A) = H_R \Rightarrow H_K$ und H_R transform into each other

ii) Preparation: $$i\partial_t \psi_{K,R} = H_{K,R}\psi_{K,R}, \quad \begin{cases} \psi_K(t) = U_K \psi_K(0) \\ \psi_R(t) = U_R \psi_R(0) \end{cases}$$

$$\Rightarrow \begin{cases} i\partial_t U_K = H_K U_K, & U_K(t,t) = \mathbb{1} \\ i\partial_t U_R = H_R U_R, & U_R(t,t) = \mathbb{1} \end{cases}$$

Goal: Show that $\underbrace{U_K(t,s)}_{=:\,LHS} = \underbrace{e^{-ie\Lambda(t)} U_R(t,s)\, e^{ie\Lambda(s)}}_{=:\,RHS}$

Methodology: Show that U_K, U_R fulfill the same Diff eq with same initial conditions.

$\rightarrow$ Compare $\partial_t LHS$, $\partial_t RHS$

- $\partial_t LHS = -i H_K U_K = -i\left(\frac{1}{2m}(p-eA)^2 - \frac{e^2}{|x|}\right)\underbrace{U_K}_{=LHS}$

- $\partial_t RHS = \partial_t\left(e^{-ie\Lambda(t)} U_R(t,s)\, e^{ie\Lambda(s)}\right)$

$$= e^{-ie\Lambda(t)}\left[-ie\frac{\partial\Lambda(t)}{\partial t} U_R + \frac{\partial U_R}{\partial t}\right] e^{ie\Lambda(s)}$$

Plugin:
- $[\Lambda, p_x] = [-\vec{A}\vec{x}, -i\partial_x] = -iA_x$

$\rightarrow [\Lambda, \vec{p}] = -i\vec{A}$

- $[\Lambda, \vec{p}^2] = \vec{p}[\Lambda,\vec{p}] + [\Lambda,\vec{p}]\vec{p} = -i\vec{p}\vec{A} - i\vec{A}\vec{p}$

$= -2i\vec{p}\vec{A}$, since $\vec{A} = \vec{A}(t)$, (no $\vec{x}$)

$[\Lambda,[\Lambda,p^2]] = -[\Lambda, 2i\vec{p}A] = -2i\,\vec{p}\underbrace{[\Lambda,\vec{A}]}_{=0} - 2i[\Lambda,\vec{p}]\vec{A}$

$= 2i\cdot i\,\vec{A}\cdot\vec{A} = -2A^2$

- $\frac{\partial\Lambda}{\partial t} = +\vec{E}(t)\cdot\vec{x}$

Contd. :

$$H_R = \frac{p^2}{2m} - \frac{e^2}{|x|} - e\vec{E}\vec{x}$$

$$= e^{-ie\Lambda(t)}\left[-ie\,\vec{E}(t)\vec{x}\,U_R - i H_R U_R\right] e^{ie\Lambda(s)}$$

$$= e^{-ie\Lambda(t)}\left[i\left(\cancel{-e\vec{E}\vec{x}} - \frac{p^2}{2m} + \frac{e^2}{|x|} + \cancel{e\vec{E}\vec{x}}\right) U_R\right] e^{ie\Lambda(s)}$$

$$= e^{-ie\Lambda(t)}\left[i\left(\frac{-p^2}{2m} + \frac{e^2}{|x|}\right) U_R\right] e^{ie\Lambda(s)}$$

$$= i\, e^{-ie\Lambda(t)}\left(\frac{-p^2}{2m} U_R\right) e^{ie\Lambda(s)} + i e^{-ie\Lambda(t)} \frac{e^2}{|x|} U_R\, e^{ie\Lambda(s)}$$

$$= i\left(e^{-ie\Lambda(t)} \frac{-p^2}{2m} e^{ie\Lambda(t)} + \underbrace{e^{-ie\Lambda(t)} \frac{e^2}{|x|} e^{ie\Lambda(t)}}_{= \frac{e^2}{|x|}}\right)\left(e^{-ie\Lambda(t)} U_R\, e^{ie\Lambda(s)}\right) = (*)$$

[plugin: Let A, B linear operators, $x \in \mathbb{R}$ (QM 1 Serie 8)

$$e^{ixA} B e^{-ixA} = \sum_{n=0}^{\infty} \frac{1}{n!}(ix)^n \mathrm{Ad}_A^n(B) = B + ix[A,B] - \frac{x^2}{2!}[A,[A,B]] - \frac{ix^3}{6}[A,[A,[A,B]]] + \dots$$
]

$$\Rightarrow \quad e^{-ie\Lambda} p^2 e^{ie\Lambda} = p^2 - ie[\Lambda, p^2] - \frac{e^2}{2}[\Lambda,[\Lambda,p^2]] + \frac{ie^3}{6}[\dots] + \dots$$

$$= p^2 - ie(-2i\vec{p}\vec{A}) - \frac{e^2}{2}(-2A^2) + \frac{ie^3}{6}\underbrace{[\Lambda, -2A^2]}_{= [-\vec{A}\vec{x}, -2A^2] = 0}$$

$$= p^2 - 2e\vec{p}\vec{A} + e^2\vec{A}^2$$

$$= (p - eA)^2$$

$$\Rightarrow (*) =$$

$$(*) = i\left(-\frac{(p-eA)^2}{2m} + \frac{e^2}{|x|}\right) e^{-ie\Lambda(t)} U_R(t,s)\, e^{ie\Lambda(s)}$$

$$= -i \underbrace{\left(\frac{(p-eA)^2}{2m} - \frac{e^2}{|x|}\right)}_{=:\ \hat{C}} \underbrace{e^{-ie\Lambda(t)} U_R(t,s)\, e^{ie\Lambda(s)}}_{=\ RHS}$$

→ We showed that:

$$\boxed{\begin{array}{ll} \cdot\ \partial_t RHS = -i\,\hat{C}\, RHS, & RHS(0,0) = \mathbb{1} \\ \cdot\ \partial_t LHS = -i\,\hat{C}\, LHS, & LHS(0,0) = \mathbb{1} \end{array}}$$

$\Rightarrow$ $RHS \equiv LHS$ since the fulfil the same diff eq with the same initial condition

i.e. $$U_K(t,s) = e^{-ie\Lambda(t)}\, U_R(t,s)\, e^{ie\Lambda(s)}$$

Heuristically: $\underbrace{H(0,A)}_{H_K} \psi_K = E\psi_K$, accept that $\psi_K \to e^{ie\Lambda}\psi_K = \psi_R$ (QM 1 serie 4) under gauge transformation

- $U_R(t,s)\,\psi_R(s) = \psi_R(t)$

$$\Rightarrow U_R\, e^{ie\Lambda(s)} \psi_K(s) = e^{-ie\Lambda(t)} \psi_K(t) \to \underbrace{e^{-ie\Lambda(t)}\, U_R\, e^{ie\Lambda(s)}}_{\downarrow} \psi_K(s) = \psi_K(t)$$

$$= U_K(t,s)\cdot \psi_K(s) = \psi_K(t)$$